



# Hydrogenation of CO<sub>2</sub> to methanol over CuCeTiO<sub>x</sub> catalysts



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## ABSTRACT

Mixed oxides of CuCeO<sub>x</sub>, CuTiO<sub>x</sub> and CuCeTiO<sub>x</sub> were prepared and evaluated for methanol synthesis *via* the hydrogenation of CO<sub>2</sub>. A significant synergistic effect was observed between CeO<sub>2</sub> and TiO<sub>2</sub> as supports. The CuCeTiO<sub>x</sub> catalyst was about 4 and 260 times more active than CuTiO<sub>x</sub> and CuCeO<sub>x</sub>, respectively, in terms of turnover frequency (TOF) values. The effect of changing the amounts of CeO<sub>2</sub>, TiO<sub>2</sub> and CuO on the catalytic performance of CuCeO<sub>x</sub> was also studied. With increasing content of CeO<sub>2</sub>, the CO<sub>2</sub> conversion firstly increased and then decreased, with the CeO<sub>2</sub>/TiO<sub>2</sub> weight ratio of 1 being optimal. An increase in the CuO content slightly enhanced the CO<sub>2</sub> conversion due to the increase of metal surface area. Kinetic experiments showed that the apparent activation barriers were lower for CO<sub>2</sub> activation and methanol synthesis over CuCeTiO<sub>x</sub> than other Cu-based catalysts.

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## 1. Introduction

The reduction of CO<sub>2</sub> emission has received significant attention because of climate change and ocean acidification related to the rising CO<sub>2</sub> concentrations in the atmosphere. The utilization of CO<sub>2</sub> by large-scale industrial conversion is more attractive among the various strategies to mitigate the CO<sub>2</sub> problem [1,2]. The direct hydrogenation of CO<sub>2</sub> to methanol has several advantages: (1) methanol is one of the top 10 petrochemicals, owning a world-wide annual production of 65 million tons [2–5]; (2) methanol is an important platform compound for the production of numerous chemicals, such as formaldehyde and acetic acid; (3) in addition to the C1 and C2 products, methanol can also be converted to olefins and aromatics (such as benzene, toluene and xylenes) through the methanol-to-olefins (MTO) and the methanol-to-aromatics (MTA) processes, respectively [1]; and (4) methanol can be directly added into gasoline, and can also be transformed to gasoline through the methanol-to-gasoline (MTG) process and to dimethylether (DME) as a diesel substitute by simple dehydration.

Among the methanol synthesis catalysts such as Cu-based catalysts, transition metal carbides (TMCs) [6–8], bimetallic catalysts

[5,9] and Au-based catalysts [10–12], Cu-based catalysts are the most widely studied and own many advantages. Apparently, Cu-based catalysts are lowest-cost compared with Au-based catalysts and bimetallic catalysts using Pd or Pt. TMCs catalysts such as Mo<sub>2</sub>C produced CO or CH<sub>4</sub> rather than methanol. Although some TMCs such as TiC showed more catalytic activity than Cu surface for methanol production [7], the difficulty in the preparation of stable and high surface area TMC powder catalysts remained a challenge.

The most studied catalyst for methanol synthesis from CO<sub>2</sub> is CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> [13,14]. The main reactions related to this process include the hydrogenation of CO<sub>2</sub>, hydrogenation of CO, water–gas shift reaction (WGS) and reverse water–gas shift reaction (RWGS) [15]. Recent studies using DFT calculations and isotope tracer method suggest that the initial hydrogenation of CO<sub>2</sub> is an important step in controlling the activity and selectivity of methanol production [16–22]. These results point out the possibilities to improve methanol synthesis by promoting the adsorption and activation of CO<sub>2</sub> over the catalysts.

The reducible oxide supports, such as TiO<sub>2</sub> [14,17,18] and CeO<sub>2</sub> [16,19–23], have been found to be beneficial for both activity and selectivity in hydrogenation reactions. Although ZrO<sub>2</sub> [14,16,18,20–26] is not generally regarded as a reducible oxide, it often shows a similar capability to create oxygen vacancies as CeO<sub>2</sub> and TiO<sub>2</sub>. The advantages of using this type of supports can be summarized to three aspects, namely enhancing the CO<sub>2</sub> adsorption, decreasing the CuO crystallite size and decreasing the H<sub>2</sub> dissociation temperature. Wang et al. [19] compared the CuO/Al<sub>2</sub>O<sub>3</sub> catalyst with CuO/Al<sub>2</sub>O<sub>3</sub>–CeO<sub>2</sub> and CuO/Al<sub>2</sub>O<sub>3</sub>–Y-doped CeO<sub>2</sub> and observed that the presence of CeO<sub>2</sub> led to a significant enhancement in both

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activity and selectivity. This enhancement could be ascribed to the synergistic effect of copper oxide and the surface oxygen vacancies of ceria by means of interfacial active centers. The methanol production activity and selectivity increase with increasing ceria loading and increasing yttria doping in ceria. Qi et al. [17] found that adding  $\text{TiO}_2$  to the  $\text{CuO}/\text{Al}_2\text{O}_3$  catalyst significantly decreased the  $\text{CuO}$  crystallite size and shifted the TPR peak toward lower temperatures.

The synergistic effect of mixed oxides has also been demonstrated. Xiao et al. [18] compared  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2\text{--ZrO}_2$  as supports for  $\text{CuO--ZnO}$  catalysts and found that both  $\text{TiO}_2$  and  $\text{ZrO}_2$  decreased the crystallite sizes of  $\text{CuO}$  and  $\text{ZnO}$  and increased the surface area of metallic  $\text{Cu}$ . They also found that  $\text{TiO}_2\text{--ZrO}_2$  mixed oxide supported  $\text{CuO--ZnO}$  catalyst had enhanced amounts of basic sites and hydrogen adsorption.

The combination of  $\text{TiO}_2$  and  $\text{CeO}_2$  as catalyst supports has shown advantages in other catalysis applications. Maciel et al. [27] studied copper catalysts supported on  $\text{CeO}_2$  and/or  $\text{TiO}_2$  for WGS. The addition of  $\text{CeO}_2$  into the  $\text{TiO}_2$  support hampered the transformation of anatase to rutile phase, and facilitated the reduction of metal species. As a result, the  $\text{CuCeTi}$  oxide catalyst showed a better activity than those using only  $\text{CeO}_2$  or  $\text{TiO}_2$  as support. Park et al. [28] studied the WGS over  $\text{M}/\text{CeO}_x/\text{TiO}_2$  ( $\text{M}=\text{Au}$ ,  $\text{Cu}$ , and  $\text{Pt}$ ) catalysts through a series of surface science experiments, and found that the  $\text{M}/\text{CeO}_x/\text{TiO}_2(1\ 1\ 0)$  surfaces showed much higher catalytic activity for  $\text{H}_2$  production than the  $\text{M}/\text{TiO}_2(1\ 1\ 0)$  surfaces. At low coverages of  $\text{Cu}$  and  $\text{CeO}_x$ ,  $\text{Cu}/\text{CeO}_x/\text{TiO}_2(1\ 1\ 0)$  is 8–12 times more active than  $\text{Cu}(1\ 1\ 1)$  or the  $\text{Cu}/\text{ZnO}$  industrial catalysts due to a strong synergistic effect between  $\text{Cu}$  and the mixed-metal oxide. The combination of  $\text{CeO}_2$  and  $\text{TiO}_2$  makes the  $\text{CeO}_x$  nanoparticles favor the +3 oxidation state [29].

The above studies suggest that  $\text{Cu}/\text{TiO}_2\text{--CeO}_2$  may be active toward  $\text{CO}_2$  conversion and can inhibit the RWGS in the hydrogenation of  $\text{CO}_2$  compared with  $\text{Cu}$  catalysts supported on a single oxide. These favorable properties have also been predicted by Graciani et al. [30] through DFT calculations and surface science experiments. Similar studies were carried out on the  $\text{Au}/\text{CeO}_2/\text{TiO}_2$  surface by Yang et al. [10], demonstrating that the  $\text{CeO}_2/\text{TiO}_2$  interface could activate  $\text{Au}$  nanoparticles to more efficiently convert  $\text{CO}_2$  molecules. In the present work, we report a novel  $\text{Cu}$ -based catalyst for methanol synthesis from  $\text{CO}_2$  utilizing a strong synergistic effect between  $\text{TiO}_2$  and  $\text{CeO}_2$ , which presents excellent activity for methanol production compared with other  $\text{Cu}$ -based catalysts. The effects of chemical compositions and preparation methods were also studied to further improve the catalytic performance. The synergistic effect was discussed in detail with a combination of catalyst characterization and catalytic evaluation experiments.

## 2. Experimental

### 2.1. Catalysts preparation

The  $\text{Cu}$  catalysts supported on  $\text{CeO}_2$  ( $\text{CuCeO}_x$ ),  $\text{TiO}_2$  ( $\text{CuTiO}_x$ ) and  $\text{CeO}_2\text{--TiO}_2$  ( $\text{CuCeTiO}_x$ ) were prepared by the co-precipitation method. An aqueous solution of copper nitrate and/or cerium nitrate was prepared as the precursor. To avoid hydrolysis, the titanium tetrachloride precursor was added into cold water dropwise with a drip speed of 6 drops/min in an ice-water bath. The precursor was subsequently added into a 10 wt% soda solution dropwise while vigorously stirring under 343 K to achieve suspension. As demonstrated by Behrens et al. [31,32], the pH value for the precipitation of metal oxides played a vital role on the microstructure and thus catalytic performance of the final products. We optimized and controlled the  $\text{CO}_3^{2+}/\text{M}$  ( $\text{M}=\text{Cu}+2\text{Ce}+2\text{Ti}$ , in mole) molar ratio as 1.2 in the precipitation. To eliminate the influence of  $\text{Na}^+$  residue, the suspension was washed using deionized water, with a volume

ratio of water to suspension of 5 for five times. The sample was then dried at 363 K for 4 h. The dried samples were ground to fine powders and calcined for 4 h in air. Various calcination temperatures have been tested and 623 K was identified as the optimized temperature to produce best catalytic performance. The  $\text{CuCeTiO}_x$  catalysts with different compositions were prepared to study the effect of composition.

For the purpose of further studying the effects of preparation method and the catalysts compositions on the catalytic properties, the  $\text{CuCeTiO}_x$  catalysts were also prepared with the sol–gel (SG) method. Typically, 10 g  $\text{Ti}(\text{OC}_4\text{H}_9)_4$ , 3 mL  $\text{CH}_3\text{COOH}$  and 40 mL  $\text{C}_2\text{H}_5\text{OH}$  were mixed under stirring to form solution A. The pH of solution A was adjusted to between 2.3 and 2.7 by  $\text{HNO}_3$ . Solution B, consisting of required amounts of cerium nitrate and copper nitrate, 3 mL distilled water and 20 mL  $\text{C}_2\text{H}_5\text{OH}$ , was added dropwise to solution A under stirring until a stable sol was formed. The sol was aged to form gel and then dried at 343 K for 72 h. The dried samples were calcined under 723 K in air for 2 h.

### 2.2. Catalytic evaluation

The prepared catalysts were tested using a fixed-bed reactor. The gases,  $\text{H}_2$  (99.995%) and  $\text{CO}_2$  (99.995%), were used without further purification. The pressure of the reactor was controlled with a backpressure regulator. For each experiment, 1.2 g of catalyst was loaded in the reactor. Before reaction, the catalyst was reduced with a stream of 5%  $\text{H}_2/\text{N}_2$  mixture by increasing the temperature to 573 K at a ramping rate of 1 K/min and holding at 573 K for 4 h. After the reduction, the temperature was decreased to 508 K and the system was pressurized to 3 MPa by feeding  $\text{CO}_2$  at 10 mL/min and  $\text{H}_2$  at 30 mL/min. The corresponding gas hourly space velocity (GHSV) was 2000 mL/(g-cat h). To obtain conversion-selectivity relationship, different GHSV values were employed by changing the gas flow and catalyst amount. In the kinetic experiments, the reaction temperatures varied from 463 K to 503 K.

The outlet stream was heated to avoid condensation and analyzed online by a gas chromatograph (GC, Techcomp, GC7980). Methanol and methane were analyzed with a flame ionization detector (FID), and  $\text{CO}$  and  $\text{CO}_2$  were analyzed using a thermal conductivity detector (TCD).

### 2.3. Catalyst characterization

The powder X-ray diffraction (XRD) patterns were recorded on an automated powder X-ray diffractometer (40 kV, 40 mA, Bruker, Model D8Avance) using a  $\text{Cu K}\alpha$  radiation source and a nickel filter in the  $2\theta$  range of  $5\text{--}90^\circ$  with step size of  $2^\circ/\text{min}$ . Raman spectra were obtained in the back-scattering configuration on a Laser Raman Spectrometer (LABRAM-HR800) using an  $\text{Ar}^+$  laser (532 nm).

The surface area (SA) and pore volume (PV) were measured by low-temperature nitrogen adsorption/desorption (77 K, Autosorb-1-C, Quantachrome Co. Ltd) using standard BET and DFT methods, respectively. Before the adsorption measurements, the sample was degassed at 573 K under vacuum for 3 h. The catalyst morphology was characterized using a scanning electron microscopy (SEM, JEOL, JSM-7401F).

The capability of  $\text{CO}_2$  adsorption was measured by  $\text{CO}_2$  temperature programming desorption ( $\text{CO}_2\text{--TPD}$ ) using a flow reactor equipped with a quadrupole mass spectrometry (QMS, Tilton Group Technology, LC-D200M PRO). For each measurement, about 50 mg of the catalyst was placed in a quartz tube reactor and outgassed at 523 K under He stream for 2 h. The sample was heated to 573 K at a ramping rate of 10 K/min in  $\text{H}_2$  atmosphere and remained for 2 h. Then the reduced sample was purged with He for 15 min, and cooled to 300 K. After that, the sample was exposed to  $\text{CO}_2$  for

20 min to adsorb CO<sub>2</sub> on the surface. This sample was then heated to 1023 K at a ramping rate of 10 K/min in He, during which the desorbed gases was subsequently detected by the MS and only the mass signal at  $m/z = 44$  was recorded as the CO<sub>2</sub> desorption profile.

The surface and bulk compositions of the catalysts were measured with X-ray photoelectron spectroscopy (XPS) and inductive-coupled plasma-atomic emission spectrum (ICP-AES, Varian, Vista-MPX), respectively. The XPS measurements were performed on a high-performance electron spectrometer (ThermoFisher, 250XI) using Al-K $\alpha$  (1486.7 eV) radiation.

The dispersion and specific (chemically active) surface area of copper were determined by N<sub>2</sub>O chemisorption using the same equipment of CO<sub>2</sub>-TPD. For each measurement, about 100 mg of the catalyst was placed in a U-tube reactor and outgassed at 523 K under He for 1 h. After cooling to room temperature, the sample was heated to 573 K at a ramping rate of 2 K/min in 10% H<sub>2</sub>/Ar mixture to completely reduce the copper. N<sub>2</sub>O chemisorption experiments showed that CeTiO<sub>x</sub> and CeO<sub>2</sub> had no reduction peaks below 573 K. Therefore, the CeTiO<sub>x</sub> and CeO<sub>2</sub> did not contribute to the measurement of the Cu metal surface area. The amount of H<sub>2</sub> consumed was monitored by TCD and denoted as  $n_0$ . Then the reduced sample was cooled and exposed to a 10% N<sub>2</sub>O/He mixture for 30 min to oxidize the surface copper. This sample was then reduced for the second time and the H<sub>2</sub> consumption was denoted as  $n_s$ . The dispersion of Cu ( $D_{Cu}$ ) was calculated as:

$$D_{Cu} = \frac{2n_s}{n_0} \times 100\%$$

The specific surface area of copper ( $S_{Cu}$ ) was calculated as:

$$S_{Cu} = \frac{w_{Cu} \times D_{Cu} \times N}{Mr_{Cu} \times 1.46 \times 10^{19}}$$

where  $w_{Cu}$  is the Cu mass fraction in the sample,  $Mr_{Cu}$  is the relative atomic mass of copper,  $N$  is the Avogadro constant, and  $1.46 \times 10^{19}$  is the number of copper atoms per square meter [33].

In order to achieve consistent sample pre-treatment, the samples for nitrogen adsorption/desorption, XPS and SEM characterizations were pretreated before the measurement. To do this, 200 mg of each sample was loaded in a quartz boat, which was then placed into a tube furnace. The sample was treated in 5% H<sub>2</sub>/N<sub>2</sub> mixture in 573 K for 4 h with a heating rate of 1 K/min. After the furnace cooled down to room temperature, the samples were passivated by 1% O<sub>2</sub>/N<sub>2</sub> mixture over-night.

### 3. Results and discussion

#### 3.1. Synergetic effect of CuCeTiO<sub>x</sub> catalysts

To investigate the synergetic effect of the CuCeTiO<sub>x</sub> catalysts, the binary oxides, 30%CuO70%TiO<sub>2</sub> (CuTiO<sub>x</sub>) and 30%CuO70%CeO<sub>2</sub> (CuCeO<sub>x</sub>), and the ternary oxides 30%CuO35%CeO<sub>2</sub>35%TiO<sub>2</sub> (CuCeTiO<sub>x</sub>) were compared. The XRD patterns of the binary and ternary oxides are shown in Fig. 1. Ti oxide remained amorphous in the CuTiO<sub>x</sub> and CuCeTiO<sub>x</sub> catalysts. This result was different from those reported by Gao et al. [34] and Huang et al. [35], who observed an anatase phase in the CuCeTiO<sub>x</sub> catalyst prepared by similar co-precipitation. The absence of crystallinity in the current samples was likely attributed to the short aging time and low calcinations temperature (623 K) used in the present work. In the CuCeO<sub>x</sub> catalyst the CeO<sub>2</sub> peaks were well characterized, while in the CuCeTiO<sub>x</sub> catalyst the CeO<sub>2</sub> peaks disappeared, suggesting the formation of a new phase consisting of the solid oxide solution of Ce and Ti. This phenomenon was consistent with previous studies of CeTiO<sub>x</sub> oxides [36,37]. The reason is that Ti<sup>4+</sup> (0.61 Å) is much smaller than Ce<sup>4+</sup> (0.99 Å), therefore a higher Ti substitution should lead to the collapse of the CeO<sub>2</sub> cubic structure and the formation

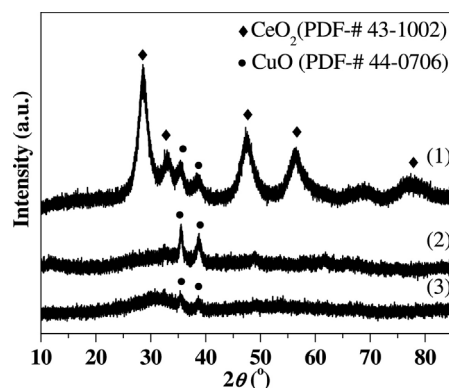


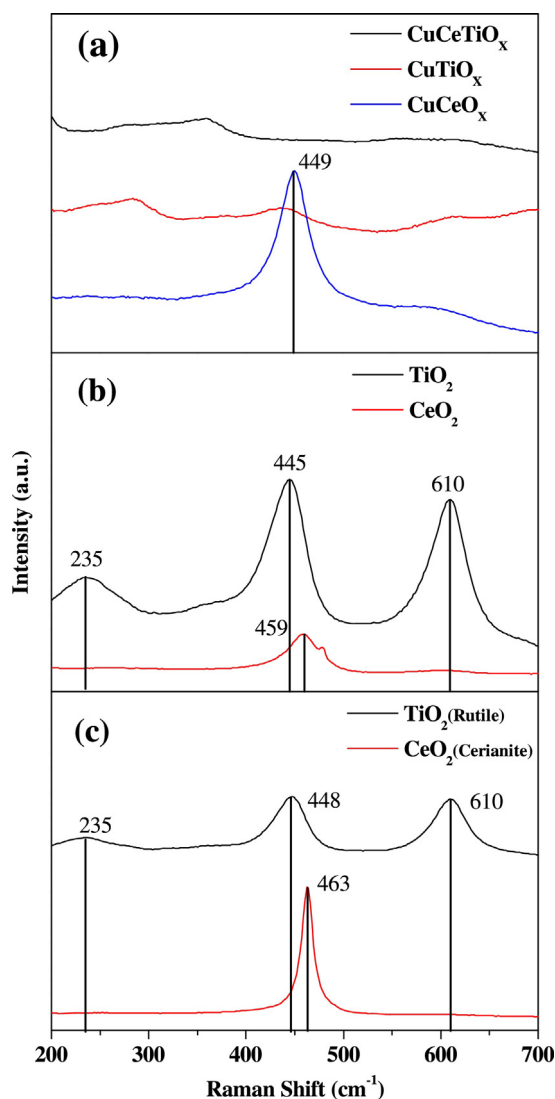
Fig. 1. XRD patterns of (1) CuCeO<sub>x</sub>, (2) CuTiO<sub>x</sub> and (3) CuCeTiO<sub>x</sub> catalysts.

of a solid solution. In several previous studies, the formation of oxide solid solution of Ce and Ti has been proven vital for the catalytic properties, especially for reactions involving CO<sub>2</sub> [37,38], mainly because of the oxygen vacancy effect. Study regarding the reduction properties of Ce–Ti mixed oxides by Li et al. [38] demonstrated that Ti ions greatly weakened the Ce–O bond in CeTiO<sub>x</sub>, making it easier to generate oxygen vacancies. Compared to CeO<sub>2</sub> and TiO<sub>2</sub>, the mixed oxides of Ce and Ti were also characterized by a much higher H<sub>2</sub> consumption peak, consistent with the generation of more oxygen vacancies by H<sub>2</sub> reduction. Sheer et al. [39] also found that the incorporation of TiO<sub>2</sub> into the CeO<sub>2</sub> lattice could promote the reduction of both surface and bulk oxygen in the CeTiO<sub>x</sub> supports for Pd/CeTiO<sub>x</sub> catalysts. The solid oxide solution created defects throughout the crystal and led to an increase in the oxygen mobility and diffusion in the lattice. The experimental results were consistent with the DFT calculations, which predicted that the introduction of Th and Zr ions into CeThO<sub>x</sub> [40] and CeZrO<sub>x</sub> [41] solid solutions significantly decreased the energies required for the oxygen vacancy formation and migration. As shown in Fig. 1, the diffraction peaks of CuO were observed in all the three samples. However, in CuCeTiO<sub>x</sub> the CuO peaks were much weaker, suggesting a higher CuO dispersion and smaller CuO crystallite on the CeTiO<sub>x</sub> support. This result could be likely ascribed to the higher surface area of the ternary oxide supports, which will be discussed later.

The Raman spectra of CuCeO<sub>x</sub>, CuTiO<sub>x</sub> and CuCeTiO<sub>x</sub> in Fig. 2 also suggest a molecular mixing of the oxides. In order to investigate the synergetic effect of the ternary oxide, TiO<sub>2</sub> and CeO<sub>2</sub> were prepared by the same co-precipitant method and characterized by Raman, then compared with commercial TiO<sub>2</sub> (rutile) and CeO<sub>2</sub> (cerianite) samples. The Raman spectrum of commercial TiO<sub>2</sub> showed three significant peaks at 235 cm<sup>−1</sup>, 448 cm<sup>−1</sup> and 610 cm<sup>−1</sup>, and the commercial CeO<sub>2</sub> sample showed one significant peak at 463 cm<sup>−1</sup>. The synthesized TiO<sub>2</sub> and CeO<sub>2</sub> samples had similar peaks compared with the commercial samples. The slight differences of the Raman shift of each peak between the commercial and synthesized samples may be ascribed to either the presence of trace amount of residual Na<sup>+</sup> or the difference in the oxide particle size. In comparison, the CuCeO<sub>x</sub>, CuTiO<sub>x</sub> and CuCeTiO<sub>x</sub> samples showed different peak distributions, in particular CuCeTiO<sub>x</sub> showed no obvious peaks in the region where the CeO<sub>2</sub> and TiO<sub>2</sub> peaks were expected, consistent with the formation of the oxide solid solution of Ce and Ti.

Another synergetic effect in the CuCeTiO<sub>x</sub> ternary oxide is the significant increase of surface area compared with the CuCeO<sub>x</sub> and CuTiO<sub>x</sub> binary oxides. The surface area of CuCeTiO<sub>x</sub> was 132 m<sup>2</sup>/g, which was about 5 times higher than that of CuCeO<sub>x</sub> and 9 times higher than that of CuTiO<sub>x</sub>. The pore volume data also showed substantial differences. The pore volume of CuCeTiO<sub>x</sub> was 0.30 cc/g,





**Fig. 2.** Raman spectra of CuCeO<sub>x</sub>, CuTiO<sub>x</sub> and CuCeTiO<sub>x</sub> catalysts (a), supports (b) and standard rutile, cerianite samples (c).

**Table 1**

Physical properties of CuCeO<sub>x</sub>, CuTiO<sub>x</sub> and CuCeTiO<sub>x</sub>.

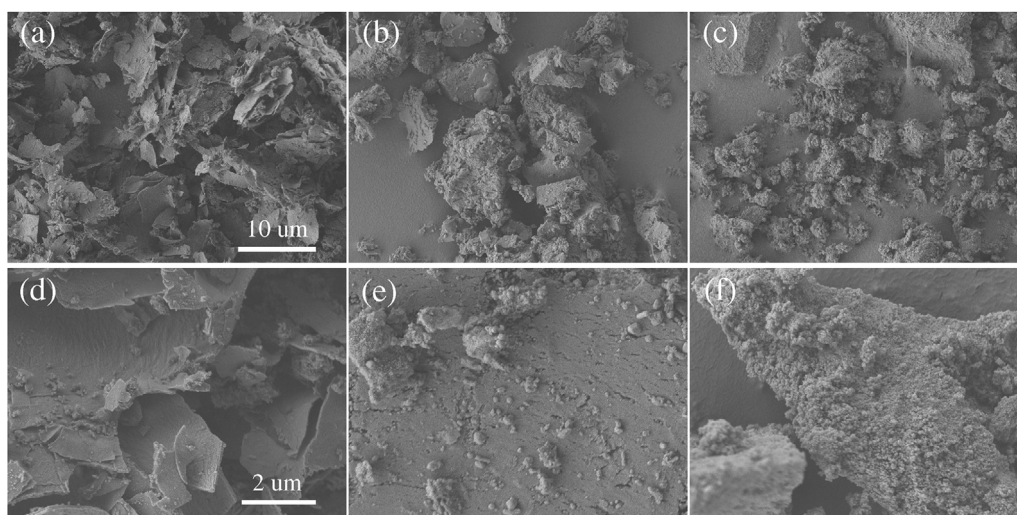
Catalysts	S.A. (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	D <sub>Cu</sub> (%)	S <sub>Cu</sub> (m <sup>2</sup> Cu/g cat)
CuCeO <sub>x</sub>	24	0.04	50.2	81
CuTiO <sub>x</sub>	14	0.02	7.0	11
CuCeTiO <sub>x</sub>	132	0.30	13.3	21

while those of CuCeO<sub>x</sub> and CuTiO<sub>x</sub> were 0.04 and 0.02 cc/g, respectively. These results are consistent with the SEM images, as shown in Fig. 3. The images in Fig. 3(a)–(c) showed that the CuCeO<sub>x</sub> sample consists of flakes of about 20 μm in size and the CuTiO<sub>x</sub> sample has a block-like morphology of similar size, while the CuCeTiO<sub>x</sub> sample had a similar block-like morphology of much smaller particle size about 5 μm. Higher amplified pictures as illustrated in Fig. 3(d)–(f) show that CuCeTiO<sub>x</sub> sample is uniquely characterized by a porous structure compared to the CuCeO<sub>x</sub> and CuTiO<sub>x</sub> samples.

The CuCeO<sub>x</sub>, CuTiO<sub>x</sub> and CuCeTiO<sub>x</sub> catalysts were compared in the evaluation for the CO<sub>2</sub> hydrogenation reaction under 3 MPa at 508 K. The results of the physical properties are listed in Table 1. The Cu dispersion and metal surface area data obtained from N<sub>2</sub>O chemisorption showed that the CuCeO<sub>x</sub> sample had the largest metal surface area of 81 m<sup>2</sup>Cu/g cat, which was over 4 times higher than the other two samples. However, this catalyst gave the lowest methanol yield, indicating that not all the exposed Cu atoms are active for CO<sub>2</sub> hydrogenation to produce methanol.

The CuCeTiO<sub>x</sub> ternary catalyst showed a much higher activity for the CO<sub>2</sub> conversion and methanol yield. Fig. 4 compares the product yields and TOF values (normalized by the surface area of Cu from N<sub>2</sub>O chemisorption) for methanol synthesis over CuCeO<sub>x</sub>, CuTiO<sub>x</sub> and CuCeTiO<sub>x</sub>. Both CuCeO<sub>x</sub> and CuTiO<sub>x</sub> showed very low activity for CO<sub>2</sub> conversion, while CuCeTiO<sub>x</sub> demonstrated a much higher conversion of CO<sub>2</sub>, approximately 7.4 and 12.0 times higher than that over CuCeO<sub>x</sub> and CuTiO<sub>x</sub>, respectively. Furthermore, the yield of methanol over CuCeTiO<sub>x</sub> was much higher than that over both CuTiO<sub>x</sub> and CuCeO<sub>x</sub>.

Comparing these three catalysts in terms of TOF values, an even more significant synergistic effect is illustrated in Fig. 4(b). The TOF over CuCeTiO<sub>x</sub> was about 4 and 260 times higher than that over CuTiO<sub>x</sub> and CuCeO<sub>x</sub>, respectively. The significant difference in the TOF values clearly indicates that the enhanced activity of CuCeTiO<sub>x</sub> is from a synergistic effect, in addition to the difference in the surface areas of different catalysts. Such significant difference means that the active sites are not the same in these three



**Fig. 3.** SEM pictures of CuCeO<sub>x</sub> (a, d), CuTiO<sub>x</sub> (b, e) and CuCeTiO<sub>x</sub> (c, f).

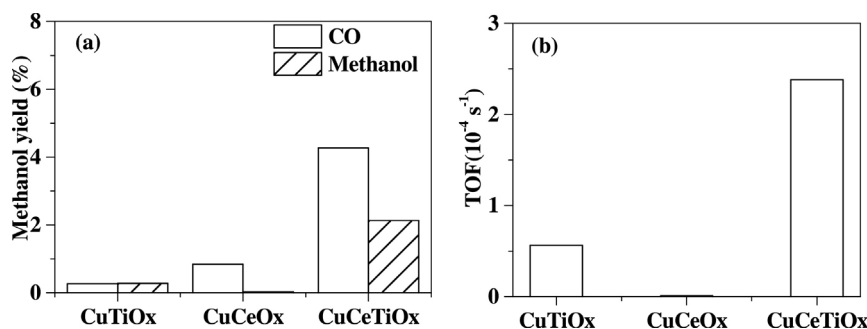


Fig. 4. Yield (a) and TOF for methanol (b) over CuCeO<sub>x</sub>, CuTiO<sub>x</sub> and CuCeTiO<sub>x</sub>.

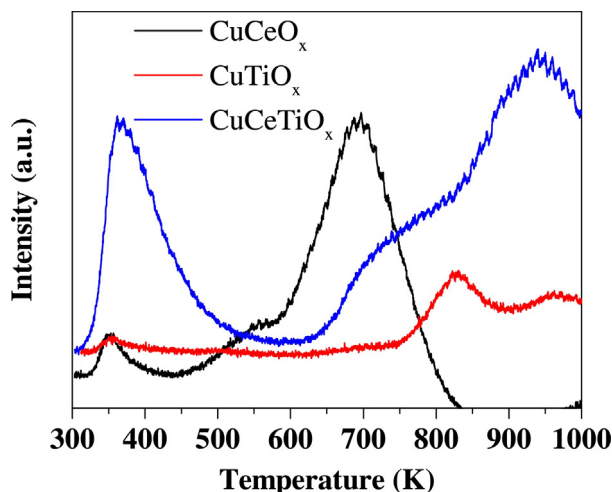


Fig. 5. CO<sub>2</sub>-TPD curves of CuCeO<sub>x</sub>, CuTiO<sub>x</sub> and CuCeTiO<sub>x</sub>.

**Table 2**  
Catalytic activity comparison of different Cu-based catalysts.

Catalysts	Methanol yield (μmol/(s g cat))	T (K)	P (MPa)	H <sub>2</sub> /CO <sub>2</sub> ratio	Ref.
CuCeTiO <sub>x</sub>	0.13	508	3	3:1	This work
CuZnO/Al <sub>2</sub> O <sub>3</sub>	0.60	503	3	3:1	[24]
Cu/SiO <sub>2</sub>	0.08	508	3	3:1	This work
Cu/Al <sub>2</sub> O <sub>3</sub>	0.10	505	3	3.8:1	[45]
Cu/ZrO <sub>2</sub>	0.17	513	8	3:1	[12]

catalysts, and that the active sites on the CuCeTiO<sub>x</sub> surface are more efficient for methanol synthesis. Combining with the XRD and Raman results, this enhancement could be explained by the formation of oxygen vacancies created by the molecular mixing of Ti and Ce in CuCeTiO<sub>x</sub>. This is consistent with previous reports that oxygen vacancies play a very important role in CO<sub>2</sub> adsorption and activation [42,43] as well as the Cu charge state [44]. This conclusion was further verified by the CO<sub>2</sub>-TPD characterization. Fig. 5 illustrates the CO<sub>2</sub> desorption curves from 300 K to 1000 K by measuring the mass signal at  $m/z = 44$  using a mass spectrometer. Only weak desorption peaks were observed between 300 and 500 K for CuCeO<sub>x</sub> and CuTiO<sub>x</sub>. In comparison, the CuCeTiO<sub>x</sub> showed a significant CO<sub>2</sub> desorption peak around 350–500 K, with a peak area approximately 12 times higher than that CuCeO<sub>x</sub>. At temperatures over 600 K, significant CO<sub>2</sub> desorption peaks appeared for all the three catalysts, and CuCeTiO<sub>x</sub> had a larger peak area than the other two catalysts. Overall, the TPD results showed that CuCeTiO<sub>x</sub> had a higher capability of CO<sub>2</sub> adsorption, especially at moderate temperature, which benefited the reduction of CO<sub>2</sub>. Table 2 compares CuCeTiO<sub>x</sub> catalyst with other Cu-based catalysts in CO<sub>2</sub> hydrogenation. The Cu/SiO<sub>2</sub> catalyst was prepared by an

**Table 3**  
Physical properties of different CuCeTiO<sub>x</sub>.

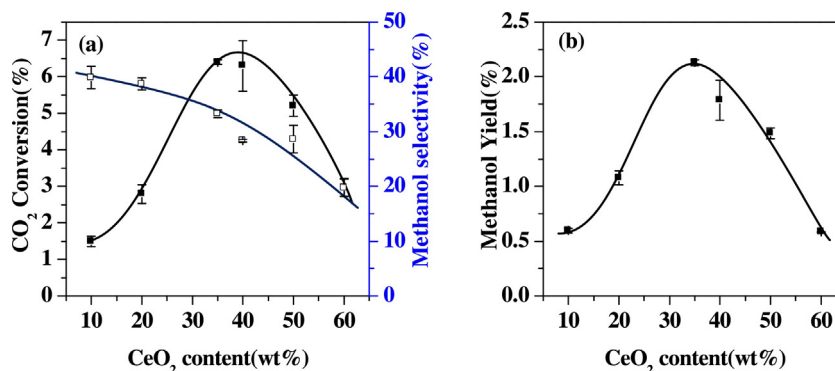
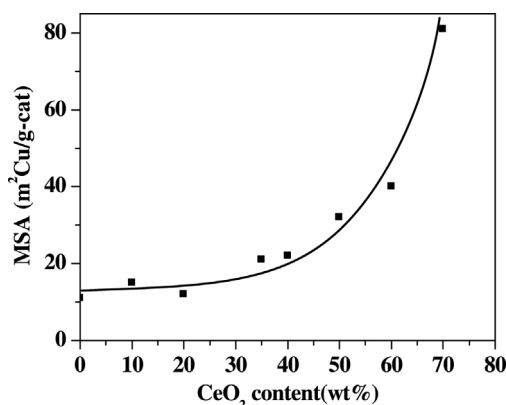
Catalysts	S.A. (m <sup>2</sup> /g)	D <sub>Cu</sub> (%)	S <sub>Cu</sub> (m <sup>2</sup> /g cat)
30Cu10Ce60Ti	161	9.0	15
30Cu20Ce50Ti	173	7.6	12
30Cu35Ce35Ti	132	13.3	21
30Cu40Ce30Ti	128	13.5	22
30Cu50Ce20Ti	107	19.8	32
30Cu60Ce10Ti	78	24.9	40
20Cu40Ce40Ti	149	11.6	13
40Cu30Ce30Ti	130	13.4	29

ammonia-evaporation method following Wang et al. [46]. Considering the addition of Zn could greatly change the Cu activity [47], Zn-free catalysts containing only Cu and oxides supports were compared. The comparison revealed that CuCeTiO<sub>x</sub> had the highest methanol yield among all catalysts, except for Cu/ZrO<sub>2</sub>. The slightly higher methanol yield on Cu/ZrO<sub>2</sub> was likely attributed to the much higher pressure. It should be pointed out that the catalytic performance of the CuTiO<sub>x</sub> catalyst in the current work is different from some of the CuTi oxide catalysts reported in the literature [48,49]. In the current study the co-precipitation method was used to prepare the CuCeTiO<sub>x</sub> mixed oxide catalysts, since it is a conventional method to obtain mixed oxide solid solution. In order to be self-consistent and to achieve a fair comparison, the CuCeO<sub>x</sub> and CuTiO<sub>x</sub> binary oxides were also prepared by co-precipitation. In comparison, the primary preparation method was impregnation for CuTi catalysts in the literatures, which are likely responsible for the observed difference in catalytic performance. Although not as competitive as the commercial CuZnAl-based catalysts, CuCeTiO<sub>x</sub> has the potential to be further improved by introducing promoters, as has been done for improving the performance of the commercial catalysts.

### 3.2. Effect of composition in CuCeTiO<sub>x</sub>

The effect of the elemental composition in the CuCeTiO<sub>x</sub> catalyst on its physical properties and catalytic performance was further studied. Several CuCeTiO<sub>x</sub> catalysts with different compositions were prepared, characterized and evaluated. As shown in Table 3, the surface area was greatly affected by the CeO<sub>2</sub> content. When the CeO<sub>2</sub> content increased from 10 wt% to 60 wt%, the surface area of CuCeTiO<sub>x</sub> decreased from 161 to 78 m<sup>2</sup>/g. Although the surface area of CuCeTiO<sub>x</sub> changed greatly with the CeO<sub>2</sub> content, all these CuCeTiO<sub>x</sub> catalysts had much higher surface areas than CuCeO<sub>x</sub> or CuTiO<sub>x</sub>. While a small amount of CeO<sub>2</sub> can prevent titania from sintering, the higher CeO<sub>2</sub> content can lead to surface area loss caused by the sintering of ceria itself. On the other hand, the presence of TiO<sub>2</sub> can inhibit the sintering of ceria, resulting in a higher surface area of the ternary oxides than the binary oxides.

Keeping the CuO content constant, the CO<sub>2</sub> conversion and methanol selectivity were affected by the CeO<sub>2</sub> content, as shown

Fig. 6. Effects of CeO<sub>2</sub> content on catalytic performance.Fig. 7. Effects of CeO<sub>2</sub> content on specific surface area of Cu.

in Fig. 6. With increasing content of CeO<sub>2</sub>, the CO<sub>2</sub> conversion first increased, reached its maximum at a CeO<sub>2</sub>:TiO<sub>2</sub> ratio of 1:1 (w/w), and then decreased with a further increase in the CeO<sub>2</sub> content. The methanol yield was 0.6% at CeO<sub>2</sub>:TiO<sub>2</sub> = 1:6 (w/w), increased to 2.1% at CeO<sub>2</sub>:TiO<sub>2</sub> = 1:1, and then decreased to 0.6% at CeO<sub>2</sub>:TiO<sub>2</sub> = 6:1.

Fig. 7 shows the variation of the metal surface area (MSA), namely specific surface area of copper, as a function of the CeO<sub>2</sub> content. With increasing CeO<sub>2</sub> content, the dispersion and surface area of Cu remained almost unchanged at CeO<sub>2</sub> content below 40%, but increased significantly with a further increase in the CeO<sub>2</sub> content. At CeO<sub>2</sub> contents below 40 wt%, the increasing CeO<sub>2</sub> content improved the Cu dispersion but decreased the overall surface area of the catalysts. At CeO<sub>2</sub> contents above 40 wt%, the Cu dispersion was greatly enhanced, thus the Cu surface area increased despite the decrease in the overall surface area. However, the higher Cu dispersion did not lead to an increase in the CO<sub>2</sub> conversion or methanol yield, suggesting that the dispersion of Cu was not the

dominant factor for this reaction and that the oxide composition might play a more important role. This also suggested that not all exposed Cu atoms had the same activity for CO<sub>2</sub> conversion.

As shown in Fig. 8, when the CuO content increased at a constant Ce/Ti ratio, the conversion of CO<sub>2</sub> increased slowly and the selectivity to methanol remained almost unchanged. The increasing CO<sub>2</sub> conversion and methanol yield can be ascribed to the increasing amount of Cu active sites introduced by the higher CuO content, which was supported by the MSA data. The unchanged selectivity for methanol suggested that the catalytic property of Cu active sites did not change with the increasing CuO content.

### 3.3. Effect of preparation methods

Sol-gel is another conventional method to prepare mixed oxides, especially for M-CeTiO<sub>x</sub> systems [50–52]. Burgos et al. [53] studied the mechanism of sol-gel transformation of Ti precursor and found that Ti alkoxides hydrolyzed at low pH formed the Ti–OH network. In the current study, it is assumed that Ce and Ti ions were hydrolyzed to form the framework at low pH during the sol-gel transformation and then the Cu ions were solidified with the evaporation of the solvents. Thus elemental distribution should differ between the bulk and surface, providing an opportunity to further study the effects of composition in CuCeTiO<sub>x</sub> on their catalytic properties.

The 30%CuO35%CeO<sub>2</sub>35%TiO<sub>2</sub> ternary oxide catalysts prepared by sol-gel (CuCeTiO<sub>x</sub>-SG) and co-precipitation (CuCeTiO<sub>x</sub>-CP) were compared. As shown in Fig. 9, the preparation methods had an important influence on the catalytic performance. The CuCeTiO<sub>x</sub>-CP catalyst showed a higher CO<sub>2</sub> conversion than CuCeTiO<sub>x</sub>-SG. However, the CuCeTiO<sub>x</sub>-SG catalyst showed a higher selectivity to methanol than CuCeTiO<sub>x</sub>-CP at the same CO<sub>2</sub> conversion. Additional studies, such as those performed for CO<sub>2</sub> conversion on supported Cu catalysts using DFT calculations and *in situ* IR measurements,

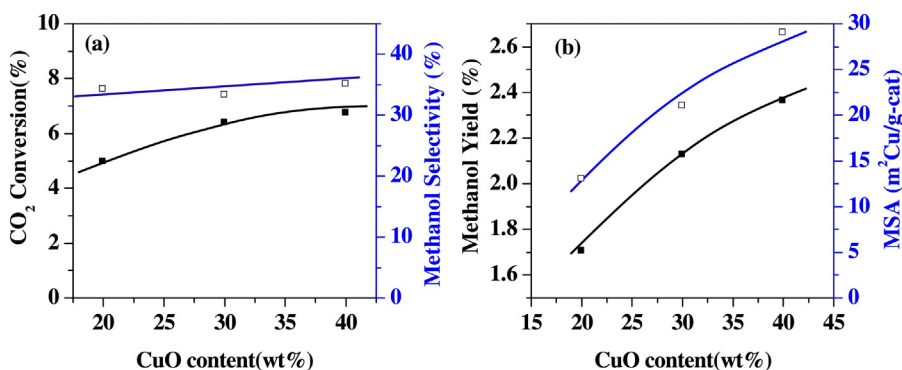


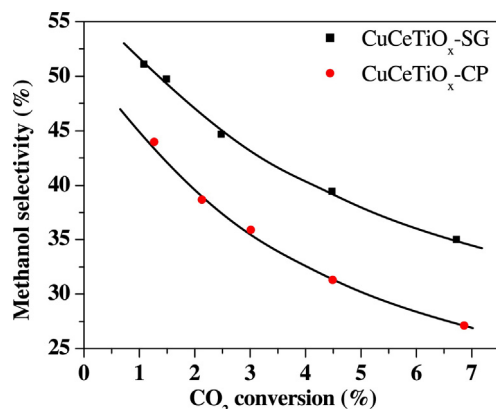
Fig. 8. Effects of CuO content on catalytic performance.

**Table 4**  
Effect of preparation methods on catalyst physical properties.

Catalysts	S.A. (m <sup>2</sup> /g)	S <sub>Cu</sub> (m <sup>2</sup> Cu/g-cat)	Compositions (CuO:CeO <sub>2</sub> :TiO <sub>2</sub> wt %)	
			Bulk	Surface
CuCeTiO <sub>x</sub> -CP	132	21	30:30:40	31:32:37
CuCeTiO <sub>x</sub> -SG	69	14	30:35:35	36:28:36

**Table 5**  
Apparent activation energy for methanol synthesis over Cu base catalysts.

Catalysts	E <sub>a</sub> -methanol (kcal/mol)	E <sub>a</sub> -CO (kcal/mol)	Experiment pressure	Ref.
CuCeTiO <sub>x</sub>	9	18	3 MPa	This work
Cu/CeO <sub>x</sub> /TiO <sub>2</sub> (1 1 0)	7	6	UHV	[30]
CeO <sub>x</sub> /Cu(1 1 1)	12–13	11	UHV	[30,60]
Cu/ZnO(0001)	16	14	UHV	[30]
Cu/ZnO(0001)	16	14	0.5 MPa	[55]
Cu(1 1 1)	25	22	UHV	[30,60]
Cu(1 1 1)	25	22	0.5 MPa	[55]
Cu/ZnO	11	31	0.7 MPa	[63]
Cu/ZrO <sub>2</sub>	10	21	3 MPa	[62]
CuO-ZnO/ZrO <sub>2</sub>	14	30	1 MPa	[64]



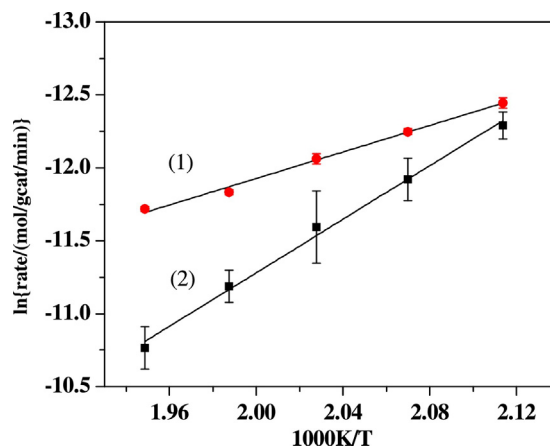
**Fig. 9.** Selectivity-conversion relationships of CuCeTiO<sub>x</sub>-SG and CuCeTiO<sub>x</sub>-CP.

[54] are necessary for a mechanistic understanding of changes in selectivity in Fig. 9.

Further characterization was carried out on these two samples and the results are listed in Table 4. The effect of preparation methods on the catalytic performance can be explained by the difference in surface composition. The XPS and ICP-AES results showed that although these two catalysts had similar bulk Cu composition, the surface Cu composition were quite different. The surface and bulk compositions were similar for CuCeTiO<sub>x</sub>-CP, while for CuCeTiO<sub>x</sub>-SG the surface Cu content was significantly higher than the bulk. The surface Cu content of CuCeTiO<sub>x</sub>-SG was 36 wt%, much higher than that of CuCeTiO<sub>x</sub>-CP. This result was consistent to the sol-gel formation mechanism discussed previously. The better selectivity for methanol over CuCeTiO<sub>x</sub>-SG could be explained by its lower surface Ce/Ti ratio than that of CuCeTiO<sub>x</sub>-CP, consistent with the effect of CeO<sub>x</sub>/TiO<sub>x</sub> shown in Fig. 6. The comparison also showed that CuCeTiO<sub>x</sub>-CP had a much larger surface area than CuCeTiO<sub>x</sub>-SG, because the drying of gel resulted in severe shrinkage and led to surface area loss [54]. These results explained why the CuCeTiO<sub>x</sub>-SG showed a higher surface Cu content, but its Cu surface area was lower than CuCeTiO<sub>x</sub>-CP.

#### 3.4. Kinetic measurements

The reaction kinetics of CO<sub>2</sub> hydrogenation to methanol has been extensively studied, especially over Cu catalysts, in the form of either model surfaces or supported catalysts. The Cu(111)



**Fig. 10.** Arrhenius plot for methanol production (1) and CO production (2) over CuCeTiO<sub>x</sub>-CP.

and CuO/ZnO(0001) surfaces were the most typical model surfaces in the kinetic study of methanol synthesis [55–61]. The current study provides a comparison of the CuCeTiO<sub>x</sub> catalyst (30%CuO35%CeO<sub>2</sub>35%TiO<sub>2</sub>, prepared by co-precipitation) with these most studied model surfaces and supported catalysts.

The apparent activation energy of methanol production was estimated over the CuCeTiO<sub>x</sub> catalyst by varying the reaction temperatures from 573 K to 613 K. The conversion was controlled below 7% in all the experiments to allow the assumption of a differential reactor. Fig. 10 shows the Arrhenius plot for methanol synthesis, giving an apparent activation energy of 9.1 ± 0.4 kcal/mol. This value is much lower than those for most commonly used Cu-based methanol synthesis catalysts, as compared in Table 5.

Surface science experiments showed that promoters and oxide supports have a significant influence on the activation energies for both methanol production and RWGS. On the Cu(111) surface, whether under ultrahigh vacuum (UHV) or high pressure of 0.5 MPa, the activation energy of methanol synthesis is about 25 kcal/mol [30,55]. The addition of ZnO decreases the activation energy from 25 to 16 kcal/mol [30,55]. The introduction of reducible oxide supports, such as ZrO<sub>2</sub> [62] and CeO<sub>2</sub> [30], also significantly decreases the activation energy. The activation energy of RWGS is slightly lower than methanol synthesis on all these model surfaces.

The experimental results of supported Cu catalysts evaluated under high pressure were quite different from surface science



studies. The activation barriers for methanol synthesis are generally about a factor of two lower than those of RWGS for all catalysts. Supported Cu catalysts such as Cu/ZnO and Cu/ZrO<sub>2</sub> also showed a lower activation energy of 8–11 kcal/mol and 10 kcal/mol, respectively. In comparison, supported Cu catalysts showed an activation energy for RWGS of 20–30 kcal/mol, which was much higher than the values from model surfaces.

In the current study, the activation energy for methanol synthesis over CuCeTiO<sub>x</sub> is  $9.1 \pm 0.4$  kcal/mol, which is lower than most catalysts listed in Table 5, and very close to that measured on the Cu/CeO<sub>x</sub>/TiO<sub>2</sub>(1 1 0) surface in UHV experiments. The activation energy for RWGS over CuCeTiO<sub>x</sub> is  $18.2 \pm 0.7$  kcal/mol, which is the lowest among the supported catalysts listed in Table 5. The lower activation energy for CO<sub>2</sub> conversion to either methanol or CO might be ascribed to the oxygen vacancies created in the solid solution of CeTiO<sub>x</sub>, which facilitated the adsorption and activation of CO<sub>2</sub> over the catalysts.

#### 4. Conclusions

Based on the results and discussion presented above, the following conclusions can be made regarding the enhanced catalytic properties of CuTiCeO<sub>x</sub> for CO<sub>2</sub> hydrogenation to methanol:

- (1) The CuCeTiO<sub>x</sub> catalyst showed a significant enhancement in activity, presenting 7 and 12 times higher CO<sub>2</sub> conversion than CuCeO<sub>x</sub> and CuTiO<sub>x</sub>, respectively. In addition, the CuCeTiO<sub>x</sub> catalyst showed over 5 times higher surface area compared with the binary oxide catalysts.
- (2) The component concentrations of CuCeTiO<sub>x</sub> had a significant influence on the catalytic performance, with a CeO<sub>2</sub>/TiO<sub>2</sub> weight ratio of 1 being optimum. The increase in the CuO content slightly increased the CO<sub>2</sub> conversion.
- (3) The preparation method also had an effect on the surface composition of CuCeTiO<sub>x</sub> and thus affected its catalytic performance.
- (4) The activation energy for methanol synthesis over CuCeTiO<sub>x</sub> was much lower than other common Cu-based catalysts, confirming the significant synergistic effect in the ternary oxide catalysts.

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